2382

High Voltage Electrical Discharge Reactions of Fats and Related Compounds

L. BORKA and O. S. PRIVETT, University of Minnesota, The Hormel Institute, Austin, Minnesota

Abstract

Studies are reported on the modification of fats and related compounds by electrical discharge reactions. Several types of fatty compounds were subjected to silent electrical discharge of the ozonizer type of 15,000 volts AC and analyzed by gas-liquid and thin-layer chromatography, infrared spectral and elemental analyses.

Evidence was obtained for a free radical reaction in accordance with the general theory of discharge reactions.

The major products of the reaction were polymers of varying degrees of complexity. Short-chain hydrocarbons were also detected. Hydrogenations via the formation of hydrogen radicals was demonstrated; branching via long-chain radical interreactions was also indicated. The incorporation of nitrogen and oxygen into polymeric products was demonstrated when the reaction was carried out in the presence of these gases.

Reaction mechanisms are proposed to explain the products formed under various conditions.

Introduction

Discharge reactions have been investigated extensively and comprehensive reviews of the subject have been published by Glockler and Lind (1), Thomas et al. (2) and Steacie (3). The most common large scale applications of discharge reactions are those of the ozone generator type (1,4) and the Cottrell precipitator (5). The latter has been used mainly for the precipitation and collection of harmful industrial smokes. Discharge reactions have been employed for the synthesis of various organic compounds (6–8), gasolenes, acetylene and lubricants (2).

In the present study the application of discharge reactions to hexadecane, methyl oleate and related compounds were investigated to define basic mechanisms and products of the reaction with fats.

Experimental

Electrical Discharge Apparatus

A schematic diagram of the apparatus for the discharge reactions is shown in Figure 1. The outer electrode of the apparatus is an aluminum sheet wrapped around the outer cylinder. The inner electrode is a copper wire, sealed in glass. This arrangement prevents contact of the sample with metal and gives a silent discharge. Alternating current (AC) high voltage was supplied from a 60 cycle, 30 ma transformer (Acme Electric Co., Chicago) with a voltage range up to 15 kv. The voltage was regulated by means of a "Variac" variable transformer connected into the primary circuit. However, unless specified differently 15 kv was employed.

The reaction tube may be loaded with sample in several ways. It may be passed into the electrical field in the form of an aerosol in helium or nitrogen, for example, or it may be applied directly on the electrode if it is a liquid or in solution if it is a solid. In the latter case the solvent evaporates and leaves the sample in the electric field as a more-less uniform layer.

Materials

Grade A Helium and "Dry-High Purity Nitrogen" purchased from the National Welding Supply, Albert Lea, Minnesota, were used as the medium for the discharge reactions.

Hexadecane (99%, olefin free) was obtained from Matheson Coleman and Bell Company, Cincinnati, Ohio. Methyl oleate, stearic acid, methyl linoleate, methyl palmitate, palmityl alcohol, methyl laurate, capryl alcohol, caprylic and methyl arachidonate were obtained from The Hormel Institute, Austin, Minnesota. All of these compounds were also greater than 99% purity except methyl arachidonate. This preparation was 95% pure; the impurities consisted of other polyunsaturated esters of lower unsaturation and a small amount of eicosapentaenoate.

Methods

Gas-liquid chromatography of methyl esters of molecular weights of the order of the compounds listed

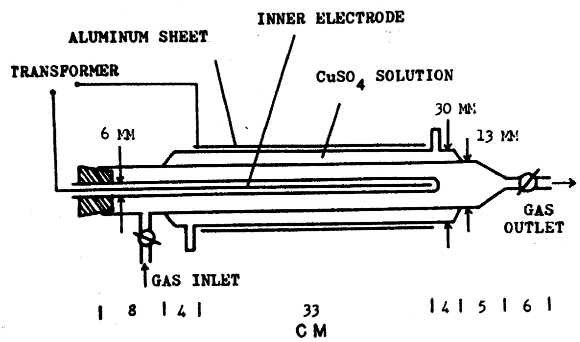

FIG. 1. Schematic diagram of the discharge reactor.

above and simple polymers thereof was carried out with an F & M Company Model 1609 flame ionization instrument equipped with a 7 ft x ¼ in. column packed with Gas-Chrom P, 100–120 mesh containing 8% by weight of ethylene glycol succinate polyester, EGSS-X (Applied Science Laboratory, State College, Pennsylvania) at 180C. A 6 ft x ¼ in. column packed with 20% Carbowax M on Chromosorb W, 60–80 mesh, was also used for some analyses.

The analysis of gaseous products was carried out by means of an Aerograph Hi-Fi 600 gas chromatograph, connected directly to the discharge reaction tube via a 1 ft x ¼ in. collection column packed with activated alumina ALCOA, 30–60 mesh. Two columns were used in the gas chromatograph; a 6 ft x ¼ in. column packed with activated alumina (ALCOA 30–60 mesh) or a 12 ft x ¼ in. column packed with 30% silicone and in Chromosorb P, 100–120 mesh. The columns were generally operated at ambient temperatures. Identification of the compounds emerging from the column was made by comparing their retention times to that of a standard mixture of gases of known composition obtained from Matheson Coleman and Bell Company. The arrangement of the equipment for the analysis of gases is illustrated in Figure 2.

The analysis of the volatile products of the discharge reactions is carried out by passing them into the collection column which may be immersed in an acetone-dry ice bath. After the reaction is completed the cold bath is removed. By allowing the column to warm up slowly, a form of temperature programming can be achieved as desorption of the gases occurs. The cold bath may also be replaced with a warm water bath (60–70C) which results in a rapid desorption and injection of the gaseous products.

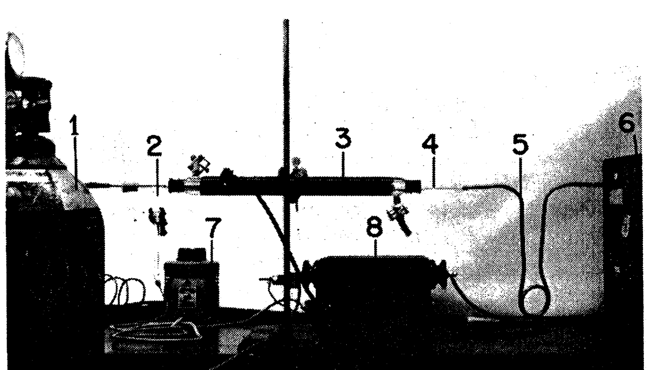

FIG. 2. Apparatus for analysis of gaseous reaction products. 1. Helium tank. 2. Gas inlet. 3. Discharge reactor. 4. Gas outlet. 5. Collection column. 6. Injection port of the gas chromatograph. 7. "Variac" variable transformer. 8. Transformer with a maximum output of 15 kv.

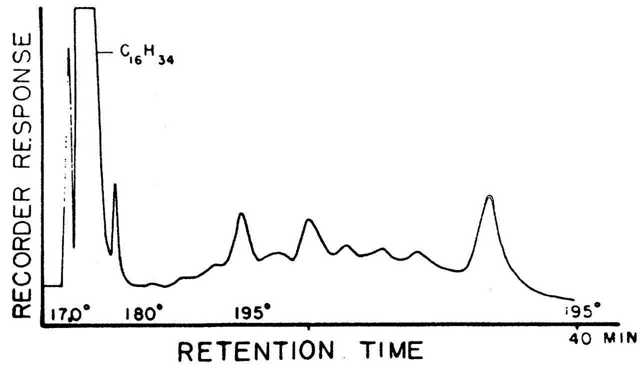

FIG. 3. Gas-liquid chromatogram of the liquid reaction products of hexadecane. Column: 6 ft x ¼ in., packed with 20% Carbowax-M on chromasorb W, 60–80 mesh. Temperature programming between 170–195C.

Thin-layer chromatography (TLC) analysis of the liquid reaction products were carried out on Silica Gel G coated plates with solvent systems as described in the respective figures.

Results

Gaseous products were produced from all of the compounds investigated. The composition of the gaseous products from experiments conducted over various compounds are summarized in Table I. In these experiments the reaction was carried out on 100 μl of sample applied directly on the electrode at 15 kv and in helium which was passed through the reactor at 80 ml per minute.

A complex mixture of nonvolatile products were formed in addition to gases. In general, when the reaction was carried out in a nitrogen atmosphere, the products could be fractionated into gaseous or volatile compounds as illustrated above, a liquid polymer fraction which was soluble in organic solvents and a solid polymer fraction which could not be dissolved in any common organic solvent. Generally the latter was isolated by filtration of the material

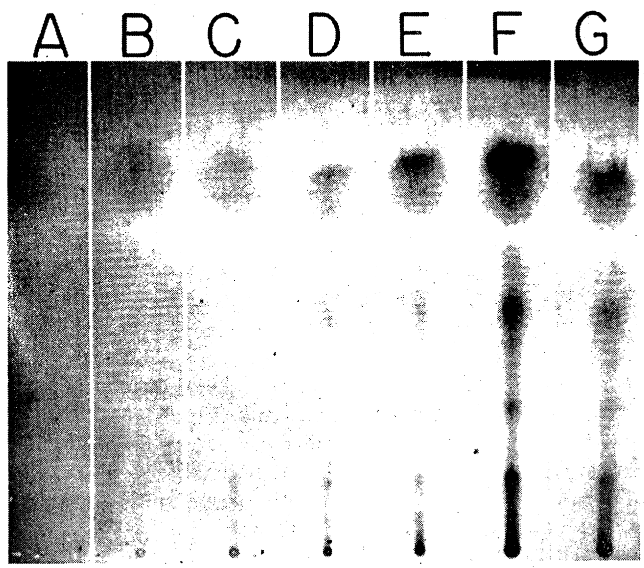

FIG. 4. Chromatoplate of high voltage treated hexadecane in nitrogen atmosphere. A: Reference hexadecane. B, C, D, E, F: Hexadecane, treated by 15 kv for 0.5, 1, 2, 5 and 15 min. G: Hexadecane, treated by 6 kv for 30 min. Coating: Silica gel G, developed in a mixture of petroleum ether (30–60C), ethyl ether (90 + 10). Charred at 180C after spraying with 70% sulfuric acid (v/v), saturated with potassium dichromate.

TABLE I
Gaseous Products of High Voltage Discharge Reactions

Compound	Time of reaction, sec.	Gases			
		% Methane	% Ethane	% Propane	% n-Butane
Hexadecane	60	67.7	17.2	4.7	10.4
Palmitic acid	90	79.3	13.7	2.7	4.3
Palmitic acid	45	78.7	12.6	4.1	4.6
Palmityl alcohol	60	83.2	11.2	2.4	3.2
Me-palmitate	15	66.7	17.3	6.5	9.5
Et-palmitate	22	75.5	13.3	4.6	6.6
Me-oleate	30	72.2	16.5	6.7	4.6

which was insoluble in pentane or chloroform. As an example of these products the above fractions were isolated from the simplest compound examined, hexadecane.

The GLC of the liquid fraction, which also contained unreacted hexadecane is shown in Figure 3. No attempt was made to identify the compounds represented by the peaks in Figure 3, however, since their retention times were longer than the parent molecule. They obviously had higher molecular weights. The same result was indicated by TLC analysis (Fig. 4). Several other aspects of the reaction are demonstrated by the TLC analysis. As the reaction progresses, more complex products are formed; however, the composition does not appear to become more complex. Four fairly well-defined fractions are formed (Fig. 4) and changing the duration of the reaction appeared only to increase the relative amounts of these fractions. The refractive index of the liquid fraction was higher than the parent substance as might be expected from the effect of branching and polymer formation.

A solid or high polymer fraction which forms on prolonged reaction may be isolated readily by virtue of its insolubility in organic solvents. A polymeric fraction may be obtained from hexadecane which is insoluble in all common organic solvents and highly resistant to the action of acids and alkali. Elemental analyses of this fraction obtained from several products are shown in Table II. The polymer formed in helium was merely a multiplication of the parent molecule. The ash content probably arose from elements of the glass as high voltage discharge also attacks glass. When the discharge reaction of hexadecane was carried out in a nitrogen atmosphere, nitrogen atoms were incorporated in the polymer as evidenced by the elemental analysis shown in Table II. The oxygen in the polymer apparently originated from traces of this gas in the nitrogen. The high percentage of oxygen in the polymer, inspite of the low concentration of oxygen in the nitrogen, is due to its lower bond energy. Thus, it was probably consumed wholly during the reaction. The properties of the polymers formed in nitrogen and helium were considerably different. Whereas the product formed in nitrogen had very strong adhesive properties and was dark in color, that formed in helium was light in color and flaky.

TABLE II
Elemental Analyses of Hexadecane-Polymers

Compound	Theory		Found					Total %
	% C	% H	% C	% H	% N	% O	% Ash	
Hexa-decane	84.87	15.13						100.00
Polymer from N_2			59.41	9.11	15.38	8.37	0.75	93.02
			59.88	9.10	12.56	10.95	1.49	93.98
Polymer from He			83.44	14.84			0.99	99.27

TABLE III
Free Radical Hydrogenation by Electrical Discharge

Compound	Increase of		
	% 18:2	% 18:1	% 18:0
Me-linoleate,		1.6	0.1
Me-oleate,			8.1
Me-linolenate,	1.05	0.03	0

The infrared spectrum of the polymer formed in helium was hardly distinguishable from the parent molecule except for evidences of branching by bands in the 8.0 μ region. The spectrum of the nitrogen containing polymer had several new adsorption bands. These bands appeared to be due to various forms of combined nitrogen, $-CH_2-NH_2$, $>CH-NH_2$, $-CH_2-NH-CH_2-$ and $-CH=NH$. This fraction also exhibited an OH band. It is not unreasonable to expect all of the above fraction groups to be present in the molecule because the polymer is not a simple multiplum of amines.

In addition to the formation of hydrocarbon radicals, hydrogen radicals were also produced in the reaction as evidences from the GLC analysis of the products formed from methyl oleate, linoleate and linolenate (Table III). The results in Table III show that lower unsaturated fatty acid esters were produced in each case. The GLC analysis was confirmed by TLC using plates coated with Silica Gel G impregnated with silver nitrate. The separation of fatty acid esters on the basis of the number and configuration of the double bond by this technique has been well demonstrated.

The hydrogenation of the double bonds does not appear to follow a probability relationship, otherwise the proportion of 18:1 and 18:0 should be 2:1 in dienes, and the proportions of 18:2, 18:1 and 18:0 would be 3:1.5:1, respectively, in trienes. It is probable that the deviations from the mathematical distribution for a random reaction is due to attack of other radicals on the double bonds.

Discussion

The present study shows that many different radicals may be produced in AC discharge reactions. These may react in a variety of ways to produce many products—gaseous, and liquid and solid polymers. Short-chain fragments, intermediate between gaseous and liquid polymers, are also probably produced. Free radicals may be visualized as being formed on electron impact with covalent bonds. The nature of the radicals and the products that are eventually formed, of course, depend on the structure of the starting materials.

With the simplest molecule studied in this work, hexadecane, the following different types of radicals appear to be produced.

a. Rupture between C—C in the chain, resulting in two free radicals:
$CH_3(CH_2)_x\cdot + \cdot(CH_2)_yCH_3$, where $x + y = 14$
eg. $CH_3(CH_2)_3\cdot + \cdot(CH_2)_{11}CH_3$

b. By breaking the C—H bond, H atom can be hit out of the molecule:

eg. $CH_3(CH_2)_3-\dot{C}H-(CH_2)_{10}CH_3 + H\cdot$

When the reaction is carried out in nitrogen which contains traces of oxygen, as in the present work, both nitrogen and oxygen radicals may be formed as well as ionic ozone.

There are numerous ways in which these radicals may recombine. Some of the more likely reactions that occur on the basis of the observations made here are as follows:

Branching:

$$CH_3(CH_2)_{11}\cdot + CH_3(CH_2)_3-\dot{C}H-(CH_2)_{10}CH_3 \rightarrow CH_3(CH_2)_3-\underset{\displaystyle (CH_2)_{11}CH_3}{\underset{|}{C}H}-(CH_2)_{10}CH_3$$

Yielding gases:

$$CH_3(CH_2)_3\cdot + \cdot H \longrightarrow n-C_4H_{10}$$

Incorporation of nitrogen and hydrogen:

$$CH_3(CH_2)_3\cdot + CH_3(CH_2)_{11}\cdot + \dot{:}N + H\cdot \longrightarrow CH_3(CH_2)_{11}-NH-(CH_2)_{11}CH_3$$

Incorporation of oxygen:

$$CH_3(CH_2)_{11}\cdot + \cdot H + :O \longrightarrow CH_3(CH_2)_{11}OH$$

Since the system is highly dynamic, no products stay in the reaction field unchanged, but undergo branching, cracking, crosslinking and end up eventually as solid polymers. The same reactions may be expected to occur with fats, and we observe the formation of solid polymers from lard. Although discharge reactions have been used for the commercial production of acetylene, gasoline, lubricants and some simple chemicals (2), a major problem has been to control them. Since it is possible to transport methyl radicals, for example, up to 37 cm (9) an important use of discharge reactions may be for the generation of radicals for use in reactions outside the electrical field.

ACKNOWLEDGMENT

One of us, L. Borka, is indebted to the Norwegian Research Council for Sciences and Humanities and the Alf Bjerckes Foundation, Oslo, Norway for a travel fellowship.

This study was supported by Agricultural Research Service, USDA Grant No. 12-14-100-7653 (73).

REFERENCES

1. Glocker, G., and S. C. Lind, The Electrochemistry of Gases and Other Dielectrics, John Wiley & Sons, New York, 1939.
2. Thomas, C. L., G. Egloff and J. C. Morell, Chem. Rev. *28*, 1 (1941).
3. Steacie, E. W. R., Atomic and Free Radical Reactions, Reinhold, New York, 1954.
4. Houzeau, A., Compt. rend. *74*, 256 (1872).
5. Cottrell, F. G., Ind. Eng. Chem. *3*, 542 (1911).
6. Miller, S. M., J. Amer. Chem. Soc. 77, 2351 (1955).
7. Oró, J., Nature, *197*, 862 (1963) and Nature *197*, 971 (1963).
8. Johnson, C. B., and A. T. Wilson, Nature *204*, 181 (1964).
9. Paneth, F., and W. Hofeditz, Ber. *62*, 1335 (1929).

[Received August 30, 1965—Accepted October 6, 1965]